

A STUDY ON THE CARBON/NO REACTION BY USING C- AND NO-ISOTOPES

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INTRODUCTION

The minimization of NO_x emission is one of the most important subjects from an environmental point of view. The following carbon-NO reaction is playing an important role in many processes like coal combustion, removal of NO_x from flue gas by activated coke, and simultaneous removal of particulate and NO_x from diesel exhaust.



Generally there is some oxygen in these practical processes, and the presence of oxygen significantly modifies the reaction rate. However, few have attempted to clarify the effect of oxygen in fundamental studies on the reaction between carbon and NO [1-3]. In a previous paper, we have investigated on the effect of oxygen during the carbon-NO reaction, where the gas analysis was performed with gas chromatography and NO_x meter [4,5]. In the present study, the reaction mechanism is studied by using mass spectroscopy which makes it possible to use isotopes to elucidate the reaction mechanism in detail.

EXPERIMENTAL

Materials. The ¹²C used in this study was phenol-formaldehyde resin (PF) char, and it was prepared as before [5]. The ¹³C was purchased from Isotec Corp. and its isotopic purity was 98.8 atom%. It was confirmed that the reactivity of these two carbons were quite similar. Two isotope gases were obtained from Isotec Corp.: ¹⁸O₂ (purity: 98 %), ¹⁵N¹⁸O (purity: 99 % for ¹⁵N and 95 % for ¹⁸O). In addition, conventional ¹⁶O₂ and ¹⁴N¹⁶O gases were used for comparison.

Procedure. In a typical kinetic experiment, about 50 mg of carbon was placed in a fixed-bed reactor made of quartz and treated under various conditions. The reaction with NO at atmospheric pressure was then carried out in the same reactor at 600°C.

Characterization of carbon. After the reaction with NO, the carbon sample was examined with a secondary ion mass spectrometer (SIMS). The spectrum was recorded with a CAMECA ims-4f using a 20 nA Cs⁺ primary ion beam.

RESULTS AND DISCUSSION

Interaction of O-containing surface species with NO. First, ¹³C was allowed to react with ¹⁶O₂ for 20 min to form ¹³C(¹⁶O), which stands for the surface species containing ¹⁶O-functionality. After ¹⁶O₂ was purged with He for 60 min, the reaction with 440 ppm ¹⁵N¹⁸O was carried out. Figure 1 shows the gas evolution profile during the reaction. ¹³C¹⁶O observed in He prior to the introduction of NO is due to the slow desorption of ¹³C(¹⁶O) complex. Upon the introduction of NO, the peaks with mass numbers of 29, 30 and 31 sharply increased and then gradually decreased. They can be unambiguously assigned to ¹³C¹⁶O, ¹⁵N₂ and ¹³C¹⁸O, respectively. The sharp increase might be due to the high reactivity of free carbon site, and also perhaps due to a temporary temperature increase by the above reaction. Not only ¹³C¹⁸O but also ¹³C¹⁶O increased at the beginning and the formation rate of these two gases were very similar. This is noteworthy because the surface species C(¹⁶O) is considered to be rather stable; it did not desorb during He-treatment for 60 min. It can thus be said that even such stable species can be removed under a gasification condition. Furthermore,

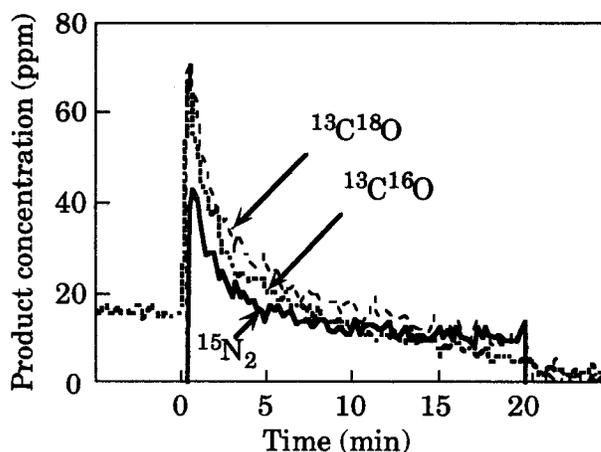


Figure 1 Product gas evolution pattern for the reaction between ¹⁶O-containing ¹³C and ¹⁵N¹⁸O. NO gas was introduced at 0 min.

it is likely that the surface oxygen complex or its neighbors are the active sites for the NO reduction reaction as suggested in our previous report [4,5].

Function of surface nitrogen species. It would be interesting to examine the possible reaction between surface nitrogen group and gaseous NO. ^{13}C or ^{12}C were treated with a mixture of $^{14}\text{N}^{16}\text{O}$ and $^{16}\text{O}_2$. By doing so, some ^{14}N as well as ^{16}O could be introduced into carbon [5]. After purging with He, the carbon was exposed to $^{15}\text{N}^{18}\text{O}$. The results are summarized in Table 1. In both cases, almost equal amounts of C^{16}O and C^{18}O were observed as in Figure 1. In the experiment with ^{13}C , we observed both mass 29 and 30. The presence of mass 30 indicated the formation of $^{15}\text{N}_2$, but the presence of mass 29 would not necessarily imply the formation of $^{14}\text{N}^{15}\text{N}$ because $^{13}\text{C}^{16}\text{O}$ also has the same mass number. In the experiment with ^{12}C , we observed only $^{15}\text{N}_2$, and no appreciable peak of mass 29 was observed. This clearly indicates that there was no N_2 which was made of one N from surface C(^{14}N) and another one from gaseous $^{15}\text{N}^{18}\text{O}$. However, this observation does not rule out the possibility of the formation of N_2 through the interaction of surface nitrogen species and gaseous NO during the actual C/NO reaction, since in the present experiment, we treated ^{14}N -containing carbon with He prior to the reaction with NO. This procedure was necessary to ensure the accuracy of quantitative analysis by mass spectroscopy. Thus we need further research to elucidate the actual reaction mechanism.

Table 1 Products in the reaction of ^{16}O -containing carbons with $^{15}\text{N}^{18}\text{O}$.

Carbon	Reactant	Products*
$^{13}\text{C}(^{16}\text{O}, ^{14}\text{N})$	$^{15}\text{N}^{18}\text{O}$	$^{13}\text{C}^{16}\text{O}, ^{13}\text{C}^{18}\text{O}, ^{15}\text{N}_2, ^{14}\text{N}^{15}\text{N}(?)$
$^{12}\text{C}(^{16}\text{O}, ^{14}\text{N})$	$^{15}\text{N}^{18}\text{O}$	$^{12}\text{C}^{16}\text{O}, ^{12}\text{C}^{18}\text{O}, ^{15}\text{N}_2$

* Only CO and N_2 are listed here.

Surface species determined by SIMS. The SIMS measurements were done with ^{13}C sample. Carbon was first treated with $^{16}\text{O}_2$ or $^{18}\text{O}_2$ for 6 min, and then with He for 10 min. These carbon will be denoted as $\text{C}(^{16}\text{O})$ and $\text{C}(^{18}\text{O})$, respectively. Then the carbon was allowed to react with 1000 ppm $^{14}\text{N}^{16}\text{O}$. Following conclusions were deduced from SIMS measurements, one example being shown in Figure 2. (1) Many peaks relating to ^{14}N -containing species were detected. Thus the trapping of nitrogen on carbon was confirmed as in the previous study [5]. (2) $^{14}\text{N}^{16}\text{O}$ and $^{14}\text{N}^{18}\text{O}$ surface species were detected in $\text{C}(^{16}\text{O})$ and $\text{C}(^{18}\text{O})$, respectively, indicating the interaction between surface oxygen containing

species with NO. (3) In the latter sample, the peak for mass 30 was not observed. This implies the dissociative adsorption of $^{14}\text{N}^{16}\text{O}$ on $\text{C}(^{18}\text{O})$ and the formation of a new bond, $^{14}\text{N}-^{18}\text{O}$. (4) Several interesting peaks like $^{13}\text{C}^{14}\text{N}_2$ and $^{14}\text{N}_2^{18}\text{O}$ were observed, although their intensities were very low. The analysis of SIMS data is not straightforward, but it can be said from this preliminary work that it has a great potential to clarify the reaction mechanism if more samples with different isotopes can be provided for analysis.

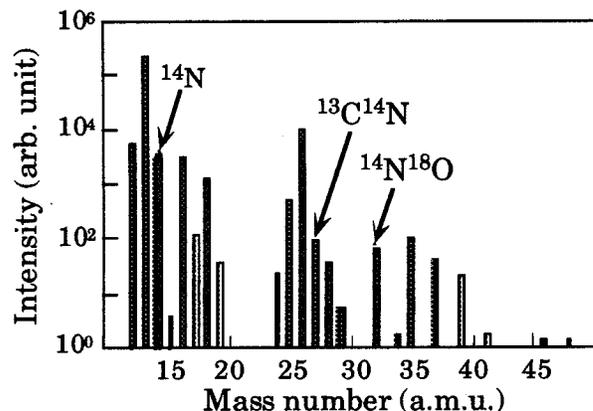


Figure 2 SIMS pattern of the carbon sample which was pretreated with $^{18}\text{O}_2$ and then gasified with $^{14}\text{N}^{16}\text{O}$.

CONCLUSIONS

Isotopes of C, O_2 , NO were used to analyze the reaction of C/NO in the presence of O_2 . We can draw the following conclusions from the present study: (1) Oxygen-containing surface complexes played an important role in the subsequent reaction with NO; (2) NO was dissociatively adsorbed on carbon and formed a new bond with surface oxygen; (3) Under the present reaction conditions, we found no evidence for the formation of N_2 , one N of which from surface and another N from NO.

REFERENCES

1. Furusawa, T.; Tsunoda, M.; Tsujimura, M.; Adschiri, T. *Fuel* **1985**, *64*, 1306.
2. Teng, H.; Suuberg, E. M.; Calo, J. M. *Energy Fuels* **1992**, *6*, 398.
3. Illan-Gomez M. J.; Linares-Solano A.; Salinas-Martinez de Lecea C.; Calo J. M. *Energy Fuels* **1993**, *7*, 146.
4. Yamashita, H.; Tomita, A.; Yamada, H. Kyotani, T.; Radovic, L. R. *Energy Fuels* **1993**, *7*, 85.
5. Suzuki, T.; Kyotani, T.; Tomita, A. *Ind. Eng. Chem. Research* **1994**, *33*, 2840.